

Delaware Valley Works
Pore Water Sampling Event
Claymont, DE and Marcus Hook, PA
January 2019



**US Army Corps
Of Engineers**
Philadelphia District



The US Army Corps of Engineers-Philadelphia District (USACE) developed a Sampling and Analysis Plan (SAP), *Pore Water Characterization, Delaware Valley Works Site Sampling and Analysis Plan (September 2018)* to direct pore water sampling and analysis activities in support of the US Environmental Protection Agency, Region 3 (EPA) related to the Delaware Valley Works facility (the Facility). The Facility is divided by Route 13 into two separate plants, commonly referred to as the “North Plant” and “South Plant,” respectively. The North Plant is located in Marcus Hook, PA and Claymont, DE while the South Plant is located almost exclusively in Claymont, DE. Currently there are multiple property owners at the Facility.

Past environmental investigations at the Facility has shown that there is a potential for arsenic and pesticides related to the Facility’s previous operations to impact the sediments of the Delaware River proximate to the shoreline of the Facility’s South Plant. To further study this condition, an SAP and associated Health and Safety Plan were prepared by USACE and submitted to EPA for review and approval prior to the start of the field investigation work. The SAP included Global Positioning System (GPS) coordinates provided by EPA for each of nine desired sampling locations. See Table 1 for the EPA requested locations and the USACE survey locations at the actual sample collection points. See Figure 1 in Appendix A for an aerial photograph depicting these locations. Due to changes in the method used to access sample locations, locations 1 through 4 were obtained using a GPS application on a smart phone.

Table 1 Sampling Locations

Location Number	EPA Coordinates	USACE Coordinates	Comment
1	39.80472719 -75.80473047	---	No sample this location
2*	39.80473047 -75.42730403	39.804683 -75.427518	GPS Error: +/- 11 ft.
3*	39.8048765 -75.42689725	39.804898 -75.426838	GPS Error: +/- 11 ft.
4*	39.80504478 -75.42651444	39.805209 -75.426211	GPS Error: +/- 14 ft.
5	39.80471878 -75.42646994	39.80478758 -75.42651406	
6	39.80457106 -75.42688847	39.80459265 -75.42686105	
7	39.8043992 -75.42740353	39.8044174 -75.42742348	
8	39.80446674 -75.42790304	39.80448418 -75.42786736	
9	39-80477307 -75.42806688	39.80484914 -75.42806914	

*Coordinates determined by smart phone GPS application.

The Philadelphia District U.S. Army Corps of Engineers (NAP) sampling team for the first phase of the sampling effort consisted of two Geo-Environmental Section members and two NAP Operations Division Boat Operators. The team traveled by boat to the Delaware Valley Works (DVW) area in Claymont, DE and the adjacent Sunoco Refinery Facility in Marcus Hook, PA on October 1 and 2, 2018 to conduct the pore water sampling at the locations shown on Figure 1.

For locations 5 through 9, the sampling team was transported from the NAP Fort Mifflin facility on the Delaware River to the sampling area via the *US Little Giant*, an NAP survey vessel capable of working in shallow water. This vessel was used as the sampling platform for four locations (5-8) and provided access to a fifth location (9).

For locations 5 through 8, the vessel was positioned as close as possible to the EPA coordinates using the on-board survey instrumentation. After positioning, the vessel was bow anchored and the sampling took place off the side on the aft deck. Six foot long pore water samplers were procured for this project due to the anticipated tidal range. The pore water sampler was attached to a stability plate at 15 centimeters from the bottom of the sampling probe. A retrieval line was attached to the plate and the top of the probe so they could be pulled aboard after the sampling. The probe was lowered to the bottom and relocated as necessary to permit the plate to rest firmly on the bottom. The interior

probe placement rod was removed and Teflon® tubing attached to the top of the probe. A disposable, 60 milliliter plastic syringe was attached to the other end of the Teflon® tubing and a vacuum placed on the system by pulling the plunger up on the syringe. The sampling tubing was clamped off (to preserve the vacuum on the system) and the water was removed from the syringe. The initial volume of water collected was discarded and assumed to be river water or a mix of river and pore water. The next water volume was tested for water quality parameters using a Myron Ultrameter Model 6P meter (Myron) to obtain field readings for conductivity, oxidation-reduction potential (ORP), pH and temperature. A sample of river water was also collected and tested using the Myron. If the parameters' results differed, the probe's water was deemed to be from pore water and sample water collection began. All water quality readings are summarized in the table included in Appendix B.

Water was collected using the syringe and emptied directly into sampling containers. Pore water extraction continued with the syringe until the flow was too restricted to justify more time on station. At the conclusion of useful sample collection, the probe was retrieved from the river using the retrieval line and stowed for transport. The vessel was then relocated to the next sampling location, or returned to Fort Mifflin. Upon completion of daily sampling activities, all probes used for sampling on that day were decontaminated at the USACE Ft. Mifflin Soils Laboratory facility. The pore water sample probes were decontaminated using water, nitric acid and acetone followed by a final water rinse.

One rinsate equipment blank was collected for the project following the decontamination process. The water used for the equipment blank was supplied by the subcontracted laboratory.

Due to the boat draft, submerged obstructions and rocks/concrete, sample location 9 was collected by running the vessel up to the DVW bulkhead remnant at the South Plant on the parcel known as Solid Waste Management Unit 9 (SWMU 9) area and off-loading the sampling team and equipment. The vessel then remained offshore until the sampling was completed and then returned to retrieve the sampling team. This change in plans was due to the safety and equipment concerns regarding the possibility of grounding the vessel against rock/debris in the area and damaging either the hull or the transducers in the hull due to wave action caused by passing vessels.

The USACE boat operators advised that they had reconnoitered the work area at low tide and found that they could not safely maneuver and keep the vessel at locations 1 through 4. This information was discussed in phone calls with EPA and a number of alternatives were offered:

1 – No Action- Stop the work and do not collect samples from locations 1 through 4;

- 2 – Access locations 2 through 4 from the Sunoco facility, do not sample location 1;
- 3- Access locations 1 through 4 by using small boats (sit on top kayaks) launched from the SWMU 9 portion of the work area or by a combination of wading in shallow water and kayaking;
- 4 – Wait for receipt and evaluation of the collected samples and determine a course of action (1 through 3, above). The laboratory turnaround time is two weeks from receipt.

On October 3, NAP and EPA met at the DVW facility and walked down the gravel road developed for well installation at the SWMU 9 portion of the facility to observe site conditions and possible access to the canal bisecting the DVW and the neighboring Sunoco facilities. It was observed that the best access for small boats would be from the gravel road before it turns upriver (east). Access issues were discussed and it was agreed that this is the best choice as it does not require access through Sunoco and did not require the additional safety equipment and personnel that Sunoco would have to request. A new Activity Hazard Analysis was developed by NAP to address the change in access to the remaining locations.

Follow-up discussions were held on October 9 with a selected course of action to be access locations 2 through 4 from the Sunoco facility and relocate location 1 to an area safely accessible from the Sunoco facility. EPA was successful in contacting the Honeywell representatives (current SWMU 9 property owners), and permission was granted to use the SWMU 9 access point.

The second phase of the sampling was conducted October 31 and November 1 to coincide with low tides during the work day. Low tides were necessary as a preliminary reconnaissance showed that the water depth and wave action encountered under high tide conditions prevented the sampling team from getting past the rip rap slope toe and into a soft sediment environ.

For sample locations 1 through 4, two sit on-top kayaks were brought to the DVW South Plant shoreline within SWMU 9 and were used to access these locations. The boats were loaded with the sampling equipment and the sampling team wearing chest waders and personal flotation devices paddled the boats to the sampling locations. The boats were beached on the rip rap shoreline, unloaded and one was then used as a sampling platform. One USACE sampler entered the water and walked out through the rip rap to find the presumed toe and a soft bottom sediment area. The actual position was determined by visual inspection of landmarks on the shore that were close to the original locations identified by the EPA. After identifying the appropriate location, the GPS-determined coordinates (presented in Table 1) were recorded, the sampling probe was inserted and sampling was conducted. One sampling modification incorporated into the phase two effort was the use of a peristaltic pump for withdrawal of the pore water rather than the

syringes, as the ability to maintain a stationary position in the river eliminated the difficulties encountered with boat drift/wave action in phase one. The peristaltic pump allowed for the withdrawal of more pore water and also enabled the sampling crew to field filter the dissolved arsenic samples using an in-line filter and preserve the dissolved arsenic samples in nitric acid preserved bottles. Filtration of the phase one dissolved arsenic samples was attempted with small cartridge filters affixed to the end of the syringe, but these filters clogged with solids almost immediately, resulting in the requirement to submit unpreserved water samples for lab filtration followed by analysis for dissolved arsenic. Another phase two modification was incorporated to address apparent memory effects with ORP readings on the Myron meter. Following all water testing, the Myron cell was filled with the pH 4 buffer which is recommended for long term storage of the meter. This change led to more consistency with the ORP readings observed for the river samples.

Preliminary review of the raw data for the pesticide samples indicated that there were significant concentrations of 4,4'-DDT, 4,4'-DDD and 4,4'-DDE (DDT series) in certain samples. EPA determined that results for these additional pesticides would be useful, and the laboratory reprocessed the available laboratory data and reported results for these additional compounds.

All changes or exceptions to the SAP for individual samples are presented below in Table 2. All other sampling activities took place as described in the SAP.

Table 2 Sample Exceptions

Item	Issue	Change	Impact
Collect full sample volumes with syringes	The pore water flow was greatly reduced or halted due to buildup of flock or sediments at the probe slots	Collected as much sample as possible until the flow was too reduced to continue sampling.	Total arsenic results are not available for Locations 5 and 6.
Collect dissolved arsenic samples	Particulate material in the water samples was too great to permit field filtration using syringes and small cartridge filters.	An unpreserved bottle was used to collect a dissolved arsenic sample. The lab was informed and requested to filter the dissolved arsenic sample in the lab.	Unpreserved sample volume for dissolved arsenic submitted for lab filtration and metals analysis for Locations 5, 6, 7, 8 and 9.

Item	Issue	Change	Impact
Lab filtration of dissolved arsenic samples	High levels of organic material in the unpreserved sample.	Lab reported that some of the samples could not be laboratory filtered.	Dissolved arsenic results are not available for Locations 5 and 6.
Sample location access	Rock, concrete and old pilings would endanger the survey vessel when approaching the shoreline at locations 1 through 4.	Access these locations via kayak/wading.	Permitted the completion of sampling after access by kayak.
GPS location by survey vessel equipment	Survey vessel could not be used to collect samples 1 through 4 and 9.	A GPS application on a smart phone was used to collect the GPS data for samples 1 through 4 and 9.	Data collected by the accuracy of the smart phone unit may not equal the survey vessel data.
Sample Location 1	Sediment material was very cohesive and very little water could be collected. Four locations were attempted.	No sample was collected	Pore water data in the vicinity of the creek mouth was not obtained.
Location 2 – pesticides analysis	Laboratory encountered significant problems with surrogate recoveries for the pesticide analysis. No additional sample volume available for re-extraction.	Pesticide analysis cancelled for this location.	Pesticide results are not available for Location 2.
Pesticide Analysis	Preliminary data review indicated that certain samples had significant concentrations of one or more of the DDT series.	Laboratory reprocessed data to include results for the DDT series.	Provided additional project information.

In addition to the equipment rinsate blank described previously, the other field Quality Control (QC) samples included a matrix spike/matrix spike duplicate (MS/MSD) pair for total arsenic collected at Location 7, an MS/MSD for dissolved arsenic and pesticides at Location 9, and a field duplicate at Location 3. A cursory review of the sample QC summary forms provided in the laboratory data packages was completed upon receipt of the data deliverables, and is summarized in Appendix D. All sample results are presented in the Data Summary Table (Table 3) provided on the following page.

Table 3 - Data Summary Table							
					Postive Result		
Client Sample ID:		LOC-001	LOC-002	LOC-003	FD-01*	LOC-004	LOC-005
Lab Sample ID:			JC77221-1	JC77181-2	JC77181-3	JC77181-1	JC75098-1
Date Sampled:			11/1/2018	10/31/2018	10/31/2018	10/31/2018	10/1/2018
Matrix:			Pore Water	Pore Water	Pore Water	Pore Water	Pore Water
Pesticides		NA	PREP				
alpha-BHC	ug/l			0.076	0.11	0.045	0.010 U
beta-BHC	ug/l			0.024	0.037	0.0080 U	0.011 U
delta-BHC	ug/l			0.0071 U	0.0071 U	0.0075 U	0.010 U
gamma-BHC (Lindane)	ug/l			0.022	0.043	0.0060 U	0.0080 U
4,4'-DDD	ug/l			0.016	0.016	0.018	0.18
4,4'-DDE	ug/l			0.0050 U	0.0050 U	0.0050 U	0.072 J
4,4'-DDT	ug/l			0.0046 U	0.0046 U	0.0075	0.27
Metals		NA					
Arsenic (Total)	ug/l		9630	6230	6120	3100	NA
Arsenic (Dissolved)	ug/l		9410	6650	5890	3850	FILT
Client Sample ID:		LOC-006	LOC-007	LOC-008	LOC-009	RINSATE	
Lab Sample ID:		JC75098-2	JC75098-3	JC75196-2	JC75196-1	JC75098-4	
Date Sampled:		10/1/2018	10/1/2018	10/2/2018	10/2/2018	10/1/2018	
Matrix:		Pore Water	Pore Water	Pore Water	Pore Water	DI Water	
Pesticides							
alpha-BHC	ug/l	0.015	0.010 U	0.014 U	0.014	0.0047 U	
beta-BHC	ug/l	0.013 J	0.011 U	0.015 U	0.0069 J	0.0050 U	
delta-BHC	ug/l	0.0088 U	0.010 U	0.014 U	0.012	0.0047 U	
gamma-BHC (Lindane)	ug/l	0.0080 J	0.0080 U	0.011 U	0.0040 U	0.0037 U	
4,4'-DDD	ug/l	8.5 J	3.2 J	5.1 J	0.32	0.0036 U	
4,4'-DDE	ug/l	2.4 J	0.17 J	0.22 J	0.032	0.0047 U	
4,4'-DDT	ug/l	20.4 J	0.41	1.1	0.025	0.0043 U	
Metals							
Arsenic (Total)	ug/l	NA	1700	504	656	1.0 J	
Arsenic (Dissolved)	ug/l	FILT	FILT	115	382	3.0 U	

Footnotes:

* - This sample is a field duplicate collected at LOC-003.

U - This analyte was not detected at or above the reported detection limit.

J - This result is an estimated value.

NA – Sample could not be collected at this location.

PREP - Sample preparation problem, pesticide results are not available.

FILT - Sample could not be filtered for dissolved arsenic analysis.

Recommendations for any future Pore Water sampling activities include the following:

- Provisions for the use of a peristaltic pump at all locations to eliminate the problems with extraction of sufficient sample volume and field filtration encountered with the syringes used throughout phase one;
- A means to stabilize the sampling platform when locations are not accessed by samplers equipped with waders and stationed within the river. Significant drift encountered with the Little Giant during the phase one sampling necessitated the use of a long length of tubing attached to the top of the sampling port. The combination of the weight of the long length of tubing and the wave action encountered in the river caused the sampling tube to move from a position that was perpendicular to the river bottom, thereby leading to potential of collecting a sample that was not at the desired depth below the surface, and;
- Improved stabilization procedures for the Myron meter to ensure that memory effects from previous samples do not lead to erroneous results.

Appendix A

Requested and Actual Sample Locations

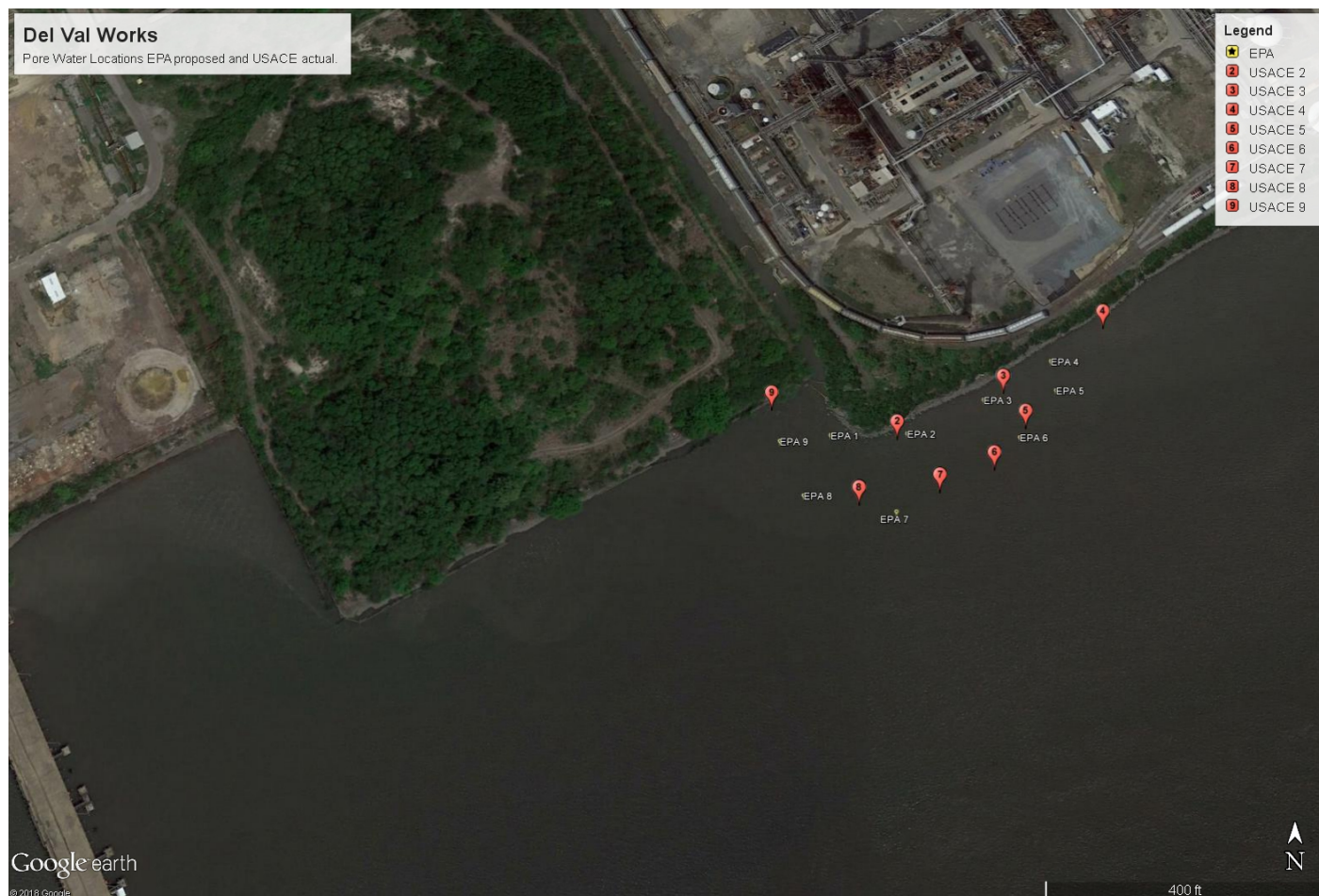


Figure 1 – EPA Requests and Actual Sample Locations

Appendix B
Water Quality Data

Location	Conductivity (uS)	ORP (mV)	pH (s.u.)	Temperature (°C)
1	No Sample Collected at this location.			
2	1940	-120	7.2	17.8
River	238	218	5.34	17
3	1560	-120	7.11	16.5
River	300	110	6.1	18.3
4	1310	-165	7.01	15.6
River	265	210	6.25	16.2
5	1001	-227	6.21	19.7
River	217	68	7.02	19.3
6	683	-215	6.72	21
River	215	68	7.17	19.7
7	1366	-190	6.7	22.4
River	227	48	7.3	20.1
8	1555	-136	7.06	23
River	241	-7	7.41	20.4
9	3480	-260	6.8	20.3
River	281	3	7.3	19.9

Appendix C

Laboratory Data Deliverables (On CD)

Appendix D

Data Review Summary

Sample Receipt and Preservation

All samples were received at the laboratory intact, at the required temperature, and under proper chain of custody. Several unpreserved samples for dissolved metals were sent to the laboratory for filtration, as described in the main portion of the report. All other samples were preserved as described in the SAP.

The original analytical request for pesticides included the four BHC isomers included in the EPA Target Compound List. Preliminary review of the pesticide data indicated that there were significant concentrations of DDT, DDD and/or DDE in certain samples. Upon further consideration of this information, EPA determined that results for these additional pesticides would be useful, and the laboratory was instructed to reprocess the available information and report results for these additional pesticides. There were no reanalysis performed, and some of these DDT, DDD or DDE results were outside of the calibration range, as described in the later portion of this summary.

Laboratory Quality Control

All samples were prepared and analyzed within the required holding times. There were no target analytes reported for any of the laboratory preparation blanks. For the sample results reported, reasonable performance was observed for all laboratory control samples, MS/MSDs, surrogate compounds, surrogate compounds, internal standards, serial dilution analysis and laboratory duplicate samples, with only occasional marginal exceedances which had no significant impact on the usability of the data.

The relative percent difference (RPD) in the dual column results for the pesticides beta-BHC in samples Location 6 and 9, gamma-BHC in sample Location 6, and DDE in samples Location 5, 7, and 8 were significantly greater than the QC limit of 40% for RPD, and these results should be considered estimated values. The RPDs for all other dual column pesticide results were within the QC limits.

Certain pesticide samples were analyzed with dilutions due to high levels of matrix interferences. These diluted analyses yielded elevated “non-detect” results for pesticides in the affected samples.

The positive results for the pesticides DDD in samples Location 7 and 8 and DDD, DDE, and DDT in sample Location 6 were outside of the instrument calibration range and should be considered estimated values.

Field Quality Control

A low concentration of total arsenic was reported for the equipment rinsate blank, but this concentration was well below the level that would lead to qualification of total arsenic results in the associated field samples.

A field duplicate sample was collected at Location 3. The precision observed for all positive results reported for this duplicate pair was within project objectives.

Conclusion

The limited review of the data did not identify any significant problems with the laboratory analysis associated with the sampling event. Certain pesticide results exhibited elevated RPDs for the dual column results reported by the laboratory, and these results should be considered estimated values. There were also results for DDT, DDE and/or DDD in three samples that were above the instrument's calibration range, and these results should be considered estimated values with a potential low bias considering the typical performance characteristics of the detector used for these analysis. All other outliers that were observed were minor exceedances having no significant impact on the data, and these results are considered usable as reported by the laboratory for this project.

Appendix E

Photographs



Assembled Pore Water Sampler showing plate, sampling tube, Teflon[®] tubing and retrieval line. Taken at Location 9.



Bottom of plate showing spiked bottom and sampling tube.



Myron Ultrameter Model 6P in use at sample Location 9.



Sample probe deployed at sample Location 9. Note that the total probe length is 6 feet (~ 183 cm), with approximately 15 cm into the sediment.



Typical kayak-based sampling. Peristaltic pump purging pore water from the sampling probe (left).



Location 1 showing the thick sediment. No pore water could be collected at this location.